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SOLAR THERMOELECTRIC GENERATOR
SYSTEM CONCEPT AND FEASIBILITY STUDY

15 MAY 1963

QUARTERLY REPORT NUMBER 5

FOR THE PERIOD

15 FEBRUARY 1963 TO 15 MAY 1963

FLIGHT ACCESSORIES LABORATORY

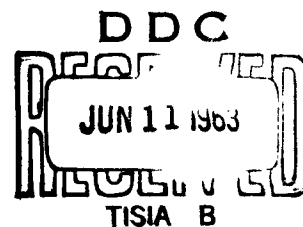
AERONAUTICAL SYSTEMS DIVISION

WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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BY WESTINGHOUSE ELECTRIC CORPORATION

AEROSPACE ELECTRICAL DIVISION

LIMA, OHIO

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The work covered by this report was accomplished under Air Force Contract AF 33(657)-8089, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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I. SUMMARY

All of the thermal storage units planned for evaluation have been tested and analyzed. The final unit was cycled for over 1000 hours. From an initial value of 92.5% lithium hydride within the container 91.1% still remained. An extension program has been finalized and work initiated on it.

II. PROJECT OBJECTIVE

The title of this project is "Solar Thermoelectric Generator System Concept and Feasibility Study." The objective is to accomplish a theoretical, analytical, and experimental applied research program to establish and prove the feasibility of a solar thermoelectric generator system concept for future advanced space flight vehicles.

A preliminary investigation including a literature survey, theoretical analysis, and component experimental evaluation is to be conducted. This preliminary investigation will result in techniques for either solving or circumventing those problems affecting the mating and design of solar thermoelectric generator system components and materials.

The test model is to have a nominal rating of 10 watts at a voltage level of approximately 7 volts when subjected to an incident solar flux level of 65 watts/ft². The environmental conditions simulate a vehicle traveling at an altitude of 300 nautical miles with an orbit of 90 minutes consisting of a 55 minute light period and a 35 minute dark period. The model will contain the following major components:

- a. Solar energy collector-concentrator
- b. Solar energy absorber
- c. Thermoelectric converter
- d. Waste heat radiator
- e. Integral, compact thermal energy storage package
- f. Electrical heat source for supplemental indoor testing

The object of the extension program is to accomplish the following:

- a. conduct extended ground evaluation of the 10 watt generator fabricated under the initial program
- b. define concept limitations and optimum configuration from the standpoint of materials parameters, power level, and cost considerations
- c. Based upon model test results and analytical results acquired, accomplish engineering design of an optimum unit directed toward solving initial operational problems, improving system efficiency and specific power to weight ratio.

III. PROJECT PROGRESS DURING REPORTING PERIOD

A. PROJECT MANAGEMENT

The fourth and final thermal storage unit has been evaluated. Over 1000 hours of time at temperature was accumulated prior to it being sent to Battelle Memorial Institute for materials evaluation. Of the 92.5% of lithium hydride initially contained, 91.1% remained. A flight weight design of a solar thermoelectric generator is being investigated. A discussion, scheduled by the NASA Sunflower project officer, was held with the personnel at TAPCO who are involved in the materials phase of the thermal storage unit. The latest test results were presented along with a review of their topical report ER-4869 entitled, "Sunflower - Boiler/Heat Storage." While in the Cleveland area we also discussed the fabrication, formability and joining of beryllium with the engineering personnel at The Brush Beryllium Company.

B. THERMAL STORAGE

Container number three was placed in the test rig for temperature cycling and it was intended to accumulate 1,000 hours of operation. Early in the program it was inadvertently overtemperated and the excess pressure generated within the container ruptured the outer wall. Some lithium hydride escaped but did not cause a fire due to the smothering effect of the thermal insulation. The failed container was delivered to Battelle Memorial Institution for investigation of the weld areas to see if this is where the failure had occurred. The container was sectioned on a Do All saw and the residual hydride in the container and the material on the outside was leached off with water. The large ring weld (see Figure 1) at the end of the container opposite the inlet end was examined. The welding scientist found that the long crack which paralleled the weld was in the base metal. The crack was located about 1/16 inch within the disk side of the weld. About 1/2 inch of incomplete fusion was found at the start-stop position in the weld, however, there was no weld failure. If anything, there was less severe cracking in this vicinity. The crack was caused by overpressure in the container which forced the re-entrant cylinder outward bending the disk end. Tensile stress opened the crack from the inside of the container. At the spun angle of the re-entrant cylinder and disk, the tensile stress was at the outside of the container but produced no cracking.

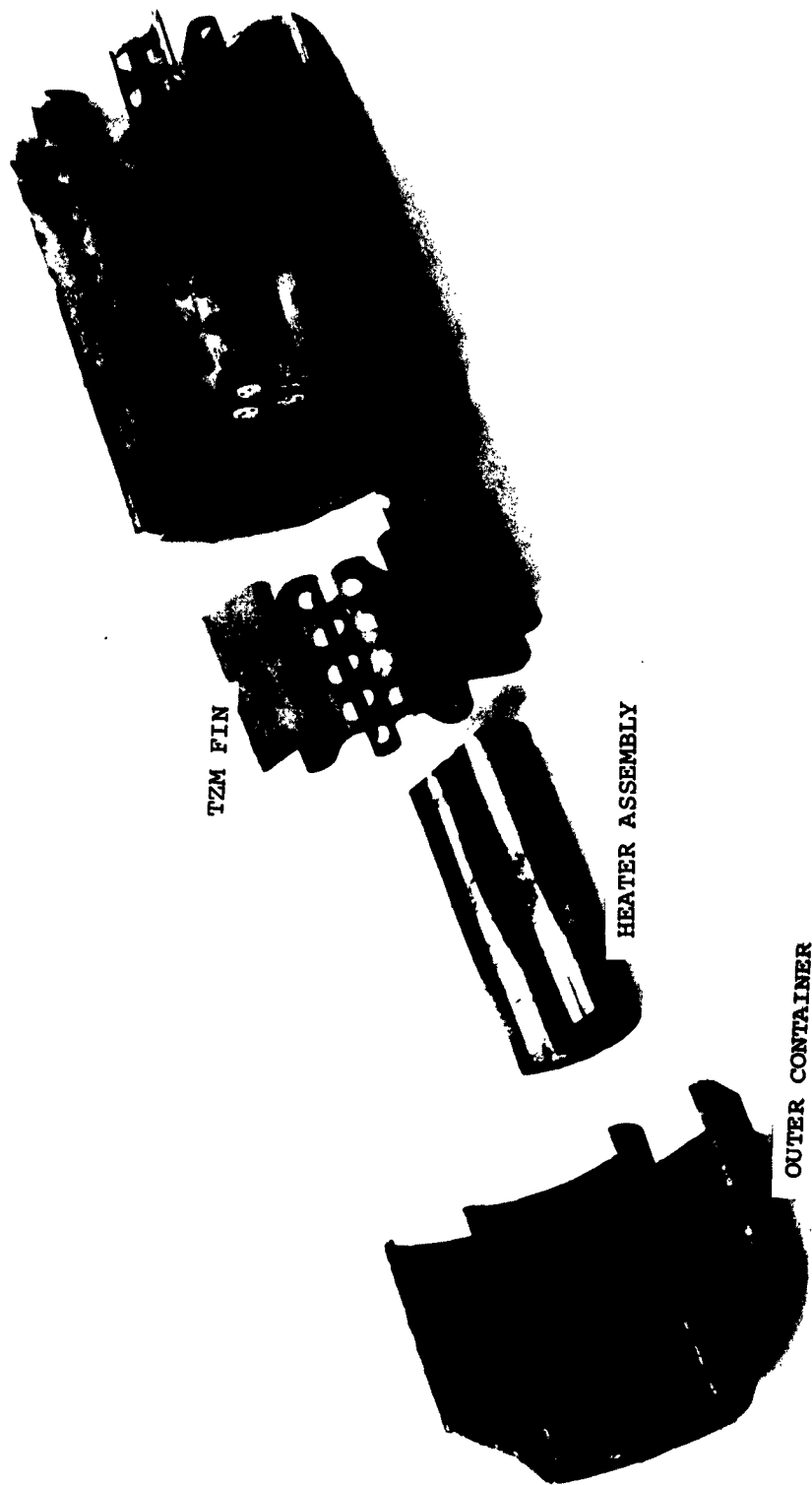


FIGURE 1 NO. 3 THERMAL STORAGE UNIT - SECTIONED

The molybdenum heat conductor had thinned slightly at the inlet end. After washing, the damp molybdenum sheet developed an odor of ammonia. Probably some nitriding of the molybdenum occurred as a result of the failure. The stainless steel parts did not have this odor.

Container number two was placed in the test rig and slightly over 1,000 hours of time at temperature was accumulated. The temperature cycle imposed went from complete melting of the lithium hydride (688°C) to complete solidification. The approximate temperature range was from 600°C to 750°C . After removing the unit from test it was sectioned longitudinally through the center axis. One half was stored under argon in a friction top can and the cross-section surface of the other half was immediately photographed in color and in black and white. The black and white photograph is designated as Figure 2. The hydride salt at the end opposite the fill tube had a blue-gray tint and in parts was fairly transparent. The salt here was more consolidated than that in other parts of the container. Toward the middle and fill end, the salt had a pinkish or amber tint. In the photograph, the narrow linear section of the molybdenum sheet is seen in one side of the container. On the other side, the section is somewhat broader and the side of one of the convolutions in the molybdenum is exposed at a void in the salt. The fill-tube stub is completely filled with salt.

Samples of hydride salt were chiseled from three positions on the right side of the container as photographed, taking the fill tube as the top. Each position represented one-third of the length of the container with the Number 1 position being nearest the fill tube. The sampling was done under a dry argon atmosphere in the same manner as for the previous containers.

After sampling, the half container was taken outdoors and the balance of the salt leached out with water. (See Figure 3) Examination of the closing weld revealed lack of fusion over the entire length of weld examined. No cracks were observed. The molybdenum heat conductor was eroded away more than the ones we examined previously. It was thinned at the fill-tube end. Complete erosion for $3/4$ to 1 inch occurred at the well side of the convolutions and the remaining metal tapered as the erosion decreased toward the outside wall where only little molybdenum had been removed. See sketch Figure 4A.

The inside walls of the container half were examined for corrosion. Etching appeared on parts of the inside walls. See Figure 4B and 4C. The wall of the center well is drawn separately to show the condition of the inside surface. The main wall of the container was roughened by etching for about $1/3$ of the distance from the fill-tube end. Then there appeared a continuous smooth band about $1/2$ inch wide which was relatively free of etching. Beyond this for the rest of the length, the wall seemed to be etched but to a lesser degree.



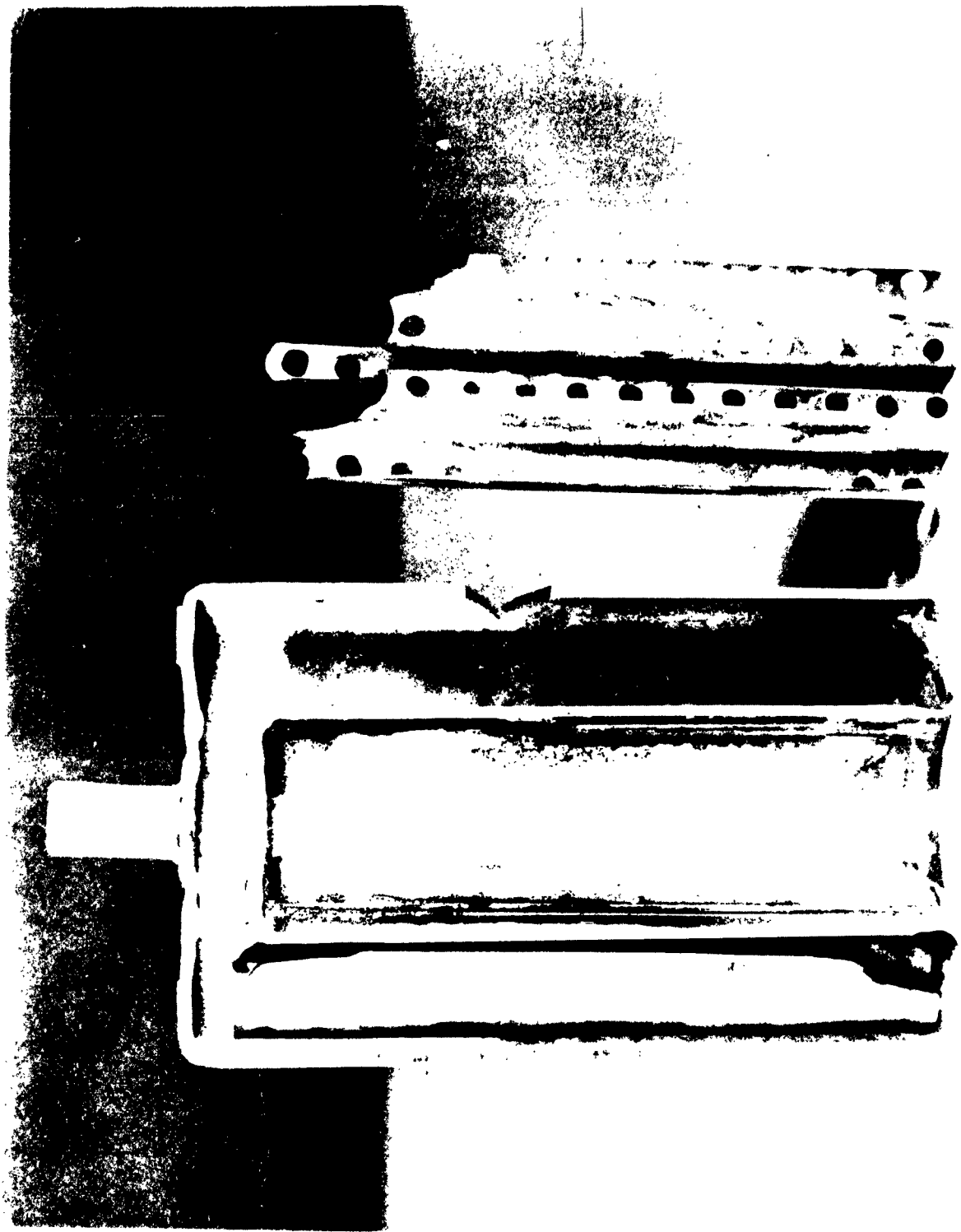
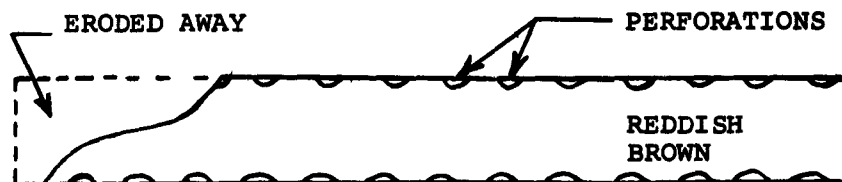
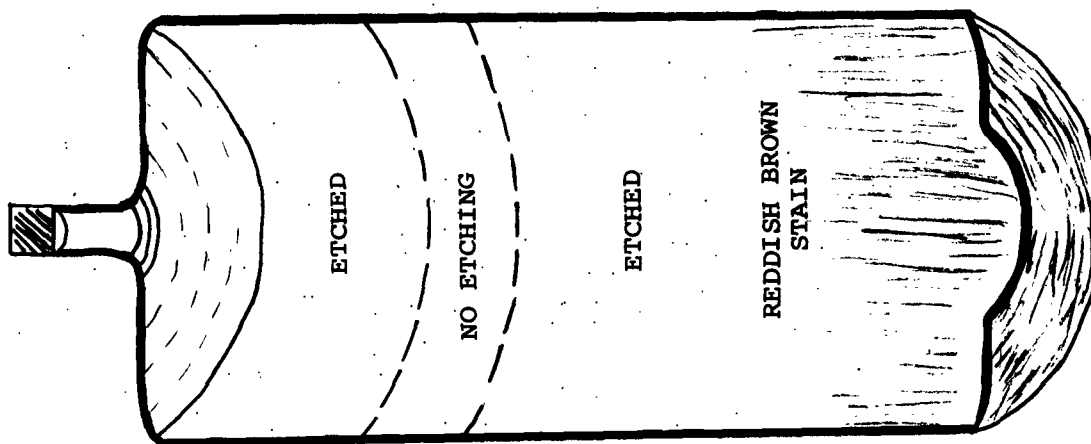


FIGURE 3 NO. 2 THERMAL STORAGE UNIT AFTER REMOVAL OF LiH

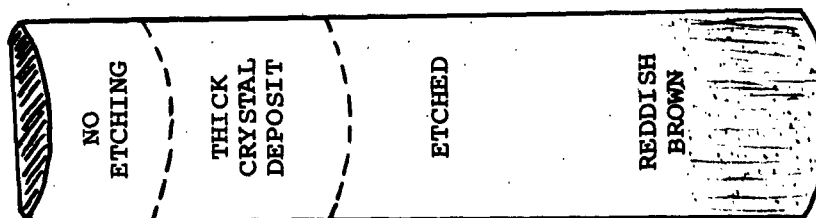


A CORRUGATED MOLYBDENUM HEAT CONDUCTOR

WELL WALL SHOWN IN FIGURE 1C



B INSIDE SURFACE OF VESSEL



C INSIDE SURFACE OF WELL WALL
WELL SECTION INVERTED

A small triangular (3/8 inch per side) specimen was cut from the outer wall of Container 2. This specimen contained residual solaramic coating on the outside and an etched surface on the inside. After polishing and etching, the cross section was examined under a microscope.

A typical field of the stainless steel in contact with lithium hydride is shown at 250X in Figure 5. A thin irregular band of a metallic phase can be seen at the surface exposed to lithium hydride. The band appeared similar to the stainless steel but might possibly be a deposit of molybdenum. Beneath the band, evidence of contamination from the lithium hydride can be seen as a constituent in the grain boundaries, especially at triple points, to a depth of about 0.003 inch (0.75 inch on the print). This can more clearly be seen at 500X as is shown in Figure 6. The heavier grain boundaries and the "Salt and pepper" appearance of the matrix to a depth of about 0.006 inch appear to be evidence of penetration of contamination from lithium hydride into the stainless steel.

The surface with the adhering solaramic diffusion barrier coating is shown at 250X in Figure 7. Here relatively very fine grains are visible just beneath the surface coating to a depth of about 0.0015 inch (0.375 inch on the print). Occasional spikes or tongues of the coating penetrate into the stainless steel to a depth of about 0.0005 inch (1/8 inch on the print). No other evidence which might be construed as contamination was found at the surface with the solaramic coating even at 500X.

For comparison, the microstructure in the core of the stainless steel is shown in Figure 8. Here the grain boundaries are shown to be thin and free of the contaminant shown near the surface exposed to lithium hydride.

The three samples of hydride salt were analyzed by the same method used for Container No. 1. The resulting hydrogen values were converted to the weight percentages of lithium hydride which follow:

CONTAINER NUMBER 2

<u>Sample Location</u>	<u>Sample Weight, mg</u>	<u>Analysis, weight per cent LiH</u>
1	22.3	91.9
2	15.8	87.4
	13.7	88.0
3	11.8	94.0



FIGURE 5 PHOTOMICRO GRAPHS OF INNER SURFACE OF NO. 2 CONTAINER 250X

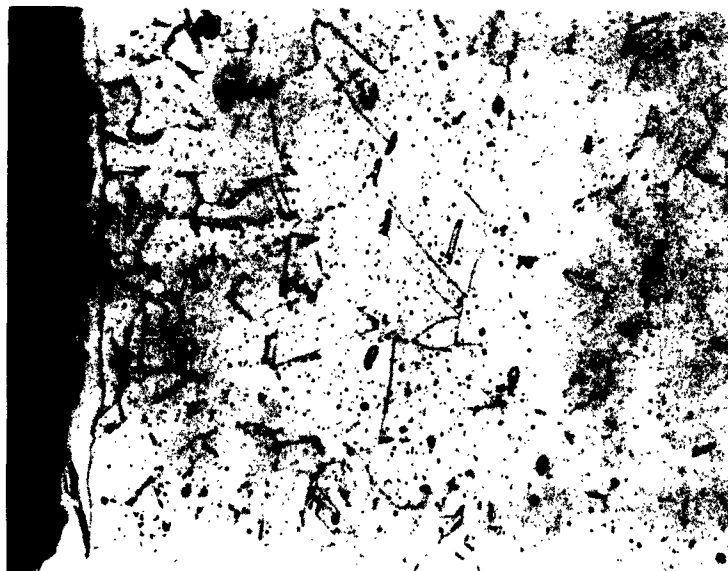


FIGURE 6 ETCHED SURFACE OF MAIN CONTAINER WALL AT 500X



FIGURE 7 CONTAINER WALL WITH SOLARAMIC COATING AT 250X



FIGURE 8 UNAFFECTED MIDDLE OF CONTAINER WALL AT 250X

Container No. 1 was loaded with lithium metal and then hydrided. It was not cycled but was analyzed as a control unit. Container No. 2 was loaded with lithium, hydrided and then cycled for 1000 hours before analysis. Container No. 5 was loaded with molten lithium hydride, cycled for 100 hours then analyzed.

The hydrogen concentration of the hydride in Container No. 2 appears to be more uniform than that reported for the hydride in Container No. 5.

The total lithium content was determined on samples of hydride from Container No. 5 and Container No. 2. A total lithium analysis for the hydride in Container No. 1 was given in our first report. Although this is an indirect method of estimating the Li_2O content of the salt, it was the only feasible approach permitted by the limited remaining funds.

RESULTS

<u>Sample Source</u>	<u>Total Lithium, Weight per cent*</u>
Container 5, location 3	79.5
Container 2, location 3	86.0
Container 1, location 3	84.5

*Average of duplicate analyses.

Both samples were chosen to resemble closely those used for the hydrogen analyses. The average of the three lithium hydride analyses reported for Container 5, location 3 is 89.8 per cent. This would represent 78.4 per cent lithium which is almost equal to the 79.5 per cent total lithium analysis. However, if one assumes that the selected sample had the lowest hydrogen analysis, 80.4 per cent (equivalent to 70.2 per cent lithium) the lithium not associated with the hydride would be 9.3 per cent as seen in the following tabulation.

	<u>Container 5, location 3</u> <u>weight per cent</u>	<u>Container 2, location 3</u> <u>weight per cent</u>
LiH	80.4	94
Equivalent Li	70.2	82.1
Total Li Analysis	79.5	86.0
Excess Li	9.3	3.9
Equivalent Li ₂ O	20.0	8.4
LiH plus Li ₂ O	100.4	102.4

This would be equivalent to 20.0 per cent Li₂O which added to the 80.4 per cent LiH gives a total of 100.4 per cent. The choice of hydride analysis is arbitrary but the low value appears to be most representative of the hydride in this region of Container 5. The tabulation also shows the calculation for Container 2, Location 3. Again the rough material balance is, within experimental error, 100 per cent.

The container numbers referred to are those reported in the fourth quarterly progress report.

C. COLLECTOR CONCENTRATOR

The collector concentrator evaluation reported in Quarterly Report No. 3 must be repeated. During the winter the surface of the metal mirror was severely pitted from corrosion. A new glass mirror manufactured by Bausch and Lomb Company has been mounted in the tracking equipment and is being calibrated. The full 5 foot diameter has been calibrated and the data being evaluated. It is now planned to calibrate the center 4 foot diameter and then the feasibility unit will be tested.

D. SYSTEM DESIGN

A flight-weight design of a solar powered thermoelectric generator is being investigated under the extension contract. A layout of a 62.5 watt design has been made. It has not as yet been determined that this will be the optimum size but is just a starting point. The concept defined by this layout will be analytically investigated to establish the optimum size from a standpoint of weight, power output, material parameters, and cost considerations. The concept has several design features which increase the power to weight ratio and performance capabilities of the device.

An improved couple has been incorporated. The hottest portion of the thermoelectric pellets are enclosed in a thin wall cavity. A diffused bonding technique is used to join the pellets and a thin wall recess provides a low resistance contact and a vapor seal. The length of the element has been reduced in order to decrease both the resistance and weight of the thermoelectric material within the couple. The length of the individual pellets has been selected to provide compatible thermal growth. This also provides a couple which operates at a current that closely approaches the desired value for each particular leg. The power to weight ratio of the thermoelectric material is greatly increased by decreasing the lengths of the pellets. The efficiency of a couple of this type closely approaches the maximum value allowed by the thermoelectric properties of the materials. In the past, couples of this type have used a 1/8" thick stainless steel hot strap. The resistance of this type of conductor was approximately 17 per cent of the couple resistance and the weight of the conductor was also an appreciable part of the total weight. The design under investigation utilizes a beryllium hot strap. In this case the resistance of the hot strap will be approximately 3.5 per cent of the couple resistance. The weight of the beryllium hot strap will be much less than the weight of stainless steel hot straps. The spring and braid assembly on the cold end of the couple used to apply a mechanical load has been eliminated. This will eliminate the temperature drop across this assembly and thus decrease the cold junction temperature. Beryllium will be used for the cold conductor material, thus weight of the cold conductor will be reduced considerably. The mechanical load required for the couple will be applied by a leaf spring located on the hot side. The temperature drop required between the thermal storage container and the thermoelectric material will be achieved across this spring.

The concept under investigation has radial fins attached to the outer shell. The previous experimental design did not have fins attached to the radiator. It should be noted that when a solar thermoelectric generator of this type is scaled up to higher power outputs the area of the outer shell approaches the area of the thermal storage container since the length of the couple does not increase with power output. Extended surface is therefore necessary to reject the waste heat at a reasonably low temperature. The computer program used to evaluate radiators for the SNAP X configuration has been revised to handle the analytical work required for the concept under investigation. A study will be made to determine the number, length, and thickness of fins required to reject the waste heat for the least weight. Beryllium will be considered for the outer shell and fin material.

A study was made to determine how the thermal impedance of the lithium hydride bath can be decreased without utilizing a large quantity of fins. In the experimental model, the weight of molybdenum (TZM) fins was approximately equal to the weight of the lithium hydride. The concept under investigation utilizes beryllium conductors in place of molybdenum conductors. The beryllium will be protected from the lithium hydride by electroplating or cladding the material with iron. This combination of materials will provide a lighter heat storage system.

In order to estimate the potential life of the present thermal storage unit, the permeability constant required for 75 per cent lithium hydride at the end of 10,000 hours operation at 700°C is given below. The rate of hydrogen flow follows the relationship:

$$Q \text{ (S.T.P.)} = \frac{KA}{d} (P_1 - P_2)$$

(S.T.P. = Standard temperature and pressure)

K = permeability constant

A = area of container = 566 CM²

d = thickness of container = 1.59 mm

P₁ = dissociation pressure of LiH @ 700°C = 35 mm = .0461 atm.

P₂ = outlet pressure = 0

Q = hydrogen flux cc/hr at standard temperature & pressure

Initial weight of H₂ = 27 grams = .0595 lbs.

Total loss H₂ allowed at the end of 10,000 hours = .015 lbs.

Volume of H₂ lost @ 0°C and 1 Atm. pressure = 2.69 ft³ = 76,700 cc

$$\frac{76,700 \text{ cc}}{10,000 \text{ Hr}} = 7.67 \frac{\text{cc}}{\text{Hr}}$$

$$Q = \text{hydrogen flux} = 7.67 \frac{\text{cc}}{\text{Hr}}$$

$$\begin{aligned}
 K \text{ (required)} &= \frac{Qd}{A (P_1 - P_2)} \\
 &= \frac{7.67 \frac{\text{cm}^3}{\text{Hr}} \times 1.59 \text{ mm}}{566 \text{ cm}^2 \times .215 \text{ atm}^{\frac{1}{2}}} \\
 &= 1.00 \times 10^{-1} \frac{\text{cm}^3 \text{ mm}}{\text{cm}^2 \text{ Hr (Atm)}^{\frac{1}{2}}}
 \end{aligned}$$

The permeability data for solaramic coating on austenitic stainless steel indicates that a lower permeability constant than $1.00 \times 10^{-1} \frac{\text{cm}^3 \text{ mm}}{\text{cm}^2 \text{ Hr (Atm)}^{\frac{1}{2}}}$ can be obtained. A value of $4 \times 10^{-2} \frac{\text{cm}^3 \text{ mm}}{\text{cm}^2 \text{ Hr (Atm)}^{\frac{1}{2}}}$

at 700°C was reported by TAPCO a division of Thompson Ramo Wooldridge, Inc. in report No. ER-4776. (This work was funded by NASA under contract NAS 5-462.) It should also be noted that the permeability of hydrogen was 10 times greater when the coating was omitted. It can be concluded from these calculations that the rate of hydrogen diffusion can be maintained within an acceptable limit by utilizing a diffusion barrier such as a solaramic coating. This coating has been extensively tested by TAPCO and has demonstrated stability for space applications for at least one year at a temperature of 1600°F. The rate of diffusion can also be controlled by the maintaining of a partial pressure of hydrogen within the chamber between the container and the radiator. For example, if this cavity is filled with a 5 per cent mixture of hydrogen and argon (5 parts of hydrogen per 100 parts of gas) the partial pressure of the hydrogen at one atm. total pressure would be 38 mm or 3 mm above the dissociation pressure of hydrogen in a lithium hydride container at 700°C. A 15 per cent mixture of hydrogen and argon would provide a partial pressure of hydrogen equal to the dissociation of hydrogen in the bath at 760°C. Since the rate of diffusion is proportional to $(P_1 - P_2)$, the rate of diffusion can be reduced significantly by maintaining a partial pressure of hydrogen in the chamber. Generators of this type are usually filled with a 15 per cent mixture of hydrogen and argon. Little effort has been made to prevent the diffusion of this hydrogen through the wall of the container. However, it is reasonable to assume that this problem can be minimized by coating the cold side of the generator with a diffusion barrier. The lower temperature of the cold wall makes this a less critical problem. The permeability constant could be from 100 to 1000 times lower at the radiator than at the wall of the lithium hydride container itself.

IV. PLANNED DIRECTIVE OF EFFORT FOR NEXT QUARTER

The feasibility model still remains to be tested using solar energy input. This will be accomplished as soon as possible. Manufacturers of solar concentrators will be contacted to acquire the latest state-of-the-art. A computer program to calculate general and system performance will be finalized.

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